STRUCTURE, PROPERTIES AND RADIATION SENSITIVITY OF ELECTRICALLY BISTABLE MATERIALS

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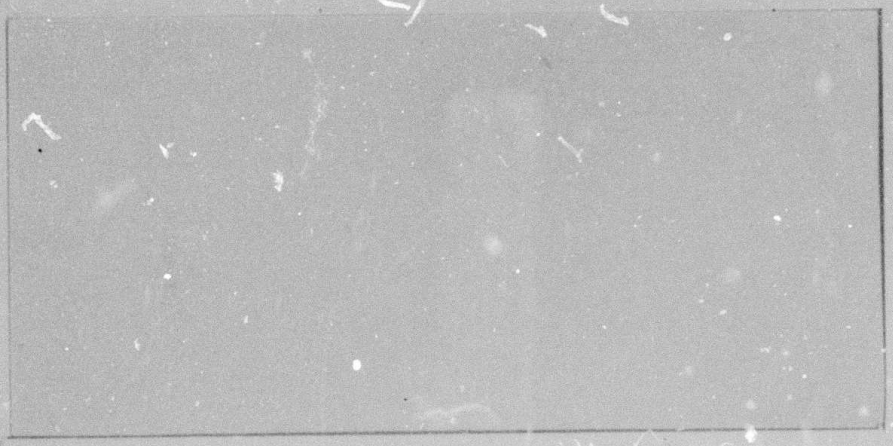

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STRUCTURE, PROPERTIES AND RADIATION SENSITIVITY OF ELECTRICALLY BISTABLE MATERIALS

Final Report

30 August 1973

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STRUCTURE, PROPERTIES AND RADIATION SENSITIVITY OF ELECTRICALLY BISTABLE MATERIALS

Final Report

30 August 1973

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ABSTRACT

This final report includes a review of the structural and electrical work carried out on amorphous semiconducting materials under contract DAHC04-7[illegible]C-0024 and summarizes results and conclusions. Also listed are technical reports, publications, theses, and personnel who have participated in this project.

STATEMENT OF PROBLEM

A major objective of this work has been to carry out metallurgical and electronic characterization of amorphous semiconductors in order to understand basic factors controlling electronic behavior and material properties of significance for device operation and stability.

STRUCTURE OF AMORPHOUS SEMICONDUCTORS

Central to any discussion of the thermal or electronic properties of amorphous semiconductors is knowledge of the atomic structure of the material. Structural analysis has therefore played an important part in the present program.

Diffraction measurements on glassy or amorphous materials yield a radial atomic distribution function, which provides in effect a spectrum of interatomic distances in the material. A major experimental difficulty is the exclusion of compton background in the x-ray case, or exclusion of inelastically scattered electrons in the case of electron diffraction. The electron diffraction measurements described in detail in earlier reports were carried out with an instrument in which inelastically scattered electrons are rejected by an electrostatic filter and intensities are measured electronically, i.e., without use of photographic plates.

Atomic radial distribution functions have been obtained for thin films of Ge_xTe_{1-x}, Ge_xSe_{1-x}, $(As_2Se_3)_x(As_2Te_3)_{1-x}$ following earlier work on Ge and GeTe. A major result is that nearest neighbor distances approximate those calculated by taking the sum of the covalent radii, and that coordination numbers are consistent with those expected if the constituent atoms possess their usual valencies.

The diffraction data therefore imply that the amorphous semiconductors examined could be regarded as primarily covalently bonded solid solutions. Calculations have shown that chemical ordering or certain types of phase separation might be exceedingly difficult to discover by diffraction measurements.

A major result has been the reinforcement of earlier work that showed that an amorphous material need not necessarily possess the same local order as crystal structures that may occur at certain compositions. Thus the work on GeSe, $GeSe_2$ gave the result that the amorphous films could be regarded as covalent solid solutions with local atomic order considerably different from those existing at these particular compositions, as concluded earlier for GeTe by various workers. In the case of the As_2Se_3-As_2Te_3 films, however, the local order in both glass and crystalline structures are similar. Comparison with curves calculated for microcrystallites of As_2Se_3 and As_2Te_3 show a nearest neighbor peak that corresponds closely with the experimental curves for the glasses, however second nearest neighbor and higher peaks are not in agreement dispelling the possibility that a significant layer structure exist in these materials.

The existence of a peak in the diffracted intensity curve at a very small angle has been taken in the literature to strongly indicate a layered structure; however calculations for small randomly oriented crystallites of As_2Se_3 and As_2Te_3 also show such a small angle peak although the hypothetic structure does not possess a layer structure extending more than one unit cell in extent.

HEAT TREATMENT

Films heated to the glass transition point inside the electron diffraction system failed to show any significant change in diffracted intensity profile, thus indicating the increased disorder due to enhanced thermal motion at the glass transition is much less than the preexisting structural disorder.

Heat treatment of films upon which a thin layer of Cu had been deposited showed very drastic changes in the amorphous diffraction pattern at temperatures not much above room temperature. The copper seems to diffuse into the films uniformly producing first a change in glassy structure and then an early devitrification. The details of this process have not been elucidated but is consistent with earlier reports on the devitrification of selenium. Reactions with aluminum or molybdenum were not found, although such reactions may possibly occur in devices where very high electric fields and high transient temperatures may enhance diffusion and promote a reaction.

Electrical measurements however indicate that molybdenum electrodes can be [illegible] by aluminum and that [illegible] changes in the material impedence could be brought about by very minor heat treatments.

CALORIMETRY

Measurements on bulk glasses in the As_2Se_3-As_2Te_3 system using a sensitive differential scanning calorimeter have established the glass transition temperature and has provided crystallization data in greater detail than previously available. The glass transition temperature varies smoothly across the compositional diagram; however

crystallization occurs by several steps depending on glass composition strongly suggesting phase separation and indicating that limited solubility of the end members occurs.

PHASE SEPARATION

Efforts to identify the occurence of phase separation in the amorphous films have been inconclusive. Evident phase separation in the films has only been observed on one rare occasion. The diffraction profile of this film was indistinguishable from those from films in which no phase separation could be resolved at all by electron microscopy. This is a major result--the diffuse diffraction pattern may be completely insensitive to certain types of phase separation. Crystallites do give very significant changes in the diffraction pattern.

Where carried out, scanning electron microscopy of fractured bulk selenium based glasses also did not reveal the presence of glass phase separation.

RADIATION TREATMENT

Work on the effects of high energy radiation on the properties of some oxide glasses was initiated early in the program but was not pursued beyond the first year or extended to the chalcogenide glasses. Several experiments on the chalcogenide materials were frustrated by reactor problems, which nullified much preradiation materials characterization effort. Discussions of the oxide glass results are to be found in previous reports.

ELECTRODE EFFECTS

A consideration of major importance in conventional semiconductor technology is that of the electronic properties of the electrode/semiconductor junction. This is a much neglected area in the case of amorphous semiconductors and for this reason an evaluation of the electrical response of materials having different electrode configurations was carried out.

Thin films were investigated in a sandwich or capacitor arrangement (as commonly employed) and in an in line, planar, arrangement in which a glass film is deposited over two electrodes separated by a gap of order 10μ.

Measurements of the frequency dependence of the electronic conductance of the material were carried out with the two arrangements and with aluminum and molybdenum electrodes.

The major result obtained was that electrode/semiconductor junction capacitance dominated the capacitor configuration results. Thus the distinction between hopping and other conduction mechanisms cannot be made without a major investigation of electrodes.

Measurements of the frequency dependent conductance showed a major change when a d.c. bias field was applied. The curves obtained in the presence of a bias field compared very closely with curves calculated for electrodes possessing Schottky barrier characteristics. The effect of the bias field changes the barrier capacitance and hence changed the a.c. measurements.

The planar, low capacitance, structure appeared to be insensitive to this effect and the results least affected by the electrodes were obtained with the planar arrangement and molybdenum electrodes. In

this way hopping conduction was clearly observed in some materials and was evidently absent in others.

Noise measurements on the two types of structures were also in agreement with this result. Changes in the noise spectrum by many orders of magnitude were observed when a bias field was applied to a device.

PERSONNEL

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Electrode Effects in Measurements on Amorphous Semiconducting Films, R. Irani and D. B. Dove.

Noise Measurements on Amorphous Semiconducting Films, R. Irani and D. B. Dove.

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Structure of Amorphous As_2Se_3-As_2Te_3 Films, J. Chang, Ph.D. Thesis, University of Florida.

Crystallization and Phase Separation in the As_2Se_3-As_2Te_3 Glass Forming System, A. Armstrong, M.Sc. Thesis, University of Florida.

Electrode Effects on Measurements on Amorphous Semiconducting Films, R. Irani, Ph.D. Thesis, University of Florida.

TECHNICAL REPORTS PUBLISHED

Report No. 1, August 6, 1970

This report describes work carried out during the first six-month period on a project directed towards a thorough electrical and metallurgical characterization of selected amorphous semiconducting materials.

Equipment for bulk glass preparation has been set up and some thin film structures have been fabricated by flash evaporation techniques. Work has commenced on local order structural measurements and electrical characterization of binary germanium tellurium alloys. It is intended that this study will be extended into more complicated systems as the project continues.

Work has commenced on systems based on the vanadium, phosphorus and potassium oxides, and a new crystalline phase has been discovered within this system. A comparative study of the electronic properties of crystalline materials and glasses having the same composition is being carried out. Finally, degradation of thin film electrodes has been observed under certain conditions and is being investigated.

Report No. 2, February 6, 1971

This report describes work carried out during the first twelve months on a project directed towards a thorough electrical and metallurgical characterization of selected amorphous semiconducting materials.

A range of semiconductors of compositions Ge_xSe_{1-x} and Ge_xTe_{1-x} have been prepared and have been examined by x-ray diffraction to verify the composition limits of the glass forming regions reported

by previous workers. Thin films have been prepared by flash evaporation of crushed bulk compounds and have been subjected to rdf analysis and electron microscopy, and several structural models are compared. Studies on the crystallization kinetics of the glasses are being carried out with particular reference to material composition. An interpretation of these initial experiments is given in terms of a possible structural model for the glasses.

The importance of crystallite size on fast neutron damage threshold in heterogeneous amorphous semiconductors is emphasized and the results of radiation experiments on vanadate glasses are discussed.

Report No. 3, September 6, 1971

This semiannaul report contains copies of papers to be published in the proceedings of the Fourth International Conference on Amorphous and Liquid Semiconductors. The first reports measurements on the thermal properties of germanium selenides using differential thermal analysis, the second describes changes in local atomic order in thin films of composition $GeTe_2$ produced by deposition conditions and heat treatment; the third paper summarizes work on the effect of microstructure on the radiation sensitivity of semiconducting glasses. Also included is a discussion of the structure of amorphous Ge_xSe_{1-x} films and their response to heat treatment. This work has been accepted by the University of Florida as partial fulfillment of the requirements of the M.S. degree of Mr. B. Molnar.

Report No. 4, February 6, 1972

This second annual report describes work carried out on the structural and electrical characterization of chalcogenide glasses.

Electron diffraction radial distribution studies have been completed in the $As_2Te_{3-x}Se_x$ system and the thermal stability of these glasses in the presence of metallic surface layers has been examined X-ray measurements on the kinetics of crystallization of bulk $GeSe_x$ glasses have been continued and diffuse scattering data have been obtained on a number of Ge-Se-As bulk glasses. Glass transition and crystallization temperatures have been observed by differential scanning calorimetry, a technique of high sensitivity.

A comparison is made between the a.c. conductivity of glasses measured with planar and sandwich electrode configurations. A significant difference has been found which may be attributed to electrode polarization effects in the sandwich structure.

Finally, a simple technique employing the decomposition of molybdenum carbonyl is described for the rapid deposition of thick refractory electrodes of good conductivity.

Report No. 5, September 6, 1972

This semiannual report contains some new measurements on the thermal stability of As_2Se_3-As_2Te_3 glasses in which multiple crystallization processes have been found by differential scanning calorimetry. X-ray work is in progress to identify the successive phases formed.

Further discussion is given of the structure of As_2Se_3 films by comparing intensity and rdf curves obtained experimentally with theoretical curves derived from a microcrystallite model. It is found that the nearest neighbor distance and average coordination is the same in the amorphous film and crystalline model. However the third prominent interatomic separation in the crystalline case is absent in

the experimental rdf. This strongly indicates that a glassy network model is more in accord with the experimental rdf than a microcrystalline model.

Continuation of the work on the interaction between As_2Se_3 and Cu support grids is strongly indicative of the formation of $Cu_{2-x}Se$ upon heat treatment. Finally a review article on electron diffraction rdfs of amorphous films prepared for the Physics of Thin Films is included.

Report No. 6, February 6, 1973

This report contains a review of work carried out on the electrical properties of contacts to chalcogenide glasses. The room temperature electrical properties of thin films of glasses have been measured with both sandwich and planar electrode configurations. Conductance and capacitance were measured versus frequency in the two cases as a function of bias voltage. A variation in response was found with bias voltage except in the case of the planar structure with molybdenum electrodes. The variation is quite consisten with a model in which Schottky barriers exist at the electrodes. These reults throw serious doubt on previous measurements of conductance and capacitance in thin films where the large changes with frequency observed were interpreted as due to material properties.

Measurements of the spectral distribution of noise currents have also been made for the two film configurations under bias and no bias conditions. All devices showed an increase in noise by several orders of magnitude when a biasing voltage was applied.